The Durability of Concrete Produced Using CO$_2$ as an Admixture

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ABSTRACT

Carbon dioxide has been investigated as a beneficial admixture to freshly mixing concrete. The reaction between the CO$_2$ and the hydrating cement forms finely distributed calcium carbonate reaction products. The carbon dioxide can be incorporated into conventional ready mixed concrete production through a simple gas system retrofit.

A comprehensive durability evaluation of carbon dioxide treated concrete was conducted. The effect of the carbon dioxide in the fresh state was assessed in terms of slump, air content, plastic density, heat of hydration and time of time. Hardened state tests included compressive strength, freeze-thaw durability (ASTM C666), linear shrinkage, rapid chloride permeability (ASTM C1202), and deicer salt scaling. Comparisons were made between a reference concrete batch, a batch that contained a conventional accelerating admixture, and a batch subjected to the carbon dioxide addition.

The concrete to carbon dioxide was found to reduce the time to initial and final set by over 20%. The CO$_2$-treated concrete had a 14% higher compressive strength than the control at one day and 10% higher strength at 3 days. Later strengths were equivalent. Durability was general unchanged although salt scaling was reduced. The carbon dioxide could be a viable non-chloride accelerator.
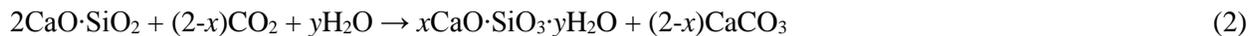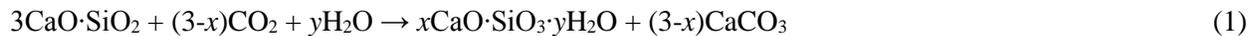
INTRODUCTION

Concrete is the most widely used manufactured material [Domone 2010]. However, carbon dioxide emissions are recognized as a significant issue relating to cement production and the growing use of concrete. It is estimated that 5% of the world's annual CO$_2$ emissions are attributable to cement production [Damtoft et al. 2008]. The cement industry recognizes a variety of approaches to reduce the emissions intensity of the cement produced and used [IEA 2009]. The thermal and electrical efficiency of cement production can be improved by deploying the best available technology in new cement plants and retrofits. Alternative and less carbon-intensive fuels can be used as the energy source. The rate of substitution in blended cements can be maximized. Finally, carbon capture and storage (CCS) can capture cement industry CO$_2$ emissions before they are released and store them permanently. The industry has previously recognized a number of approaches to reduce the emissions intensity of the cement produced and used in concrete.

It is clear, however, that practical limits on the impacts of these measures mean that it will be difficult [Barcelo 2014] to attain the industry goal to reduce emissions 50% below 2006 levels by 2050 that is outlined in the IEA & WBCSD roadmap [IEA 2009]. Innovative approaches are sought and are likely to be a part of a portfolio strategy. The biggest improvements in efficiency and cement substitution are likely already known. Future developments will result in incremental emissions improvements. Therefore, innovative approaches are sought that can be a part of a portfolio strategy.

One potential measure is to employ the beneficial reaction between carbon dioxide and freshly hydrating cement. If an industrial process could successfully use carbon dioxide as a feedstock in the production of concrete building products there could be widely distributed carbon utilization serving to effectively 'close the loop' for the carbon dioxide emitted during the cement production.

The mechanism of carbonation of freshly hydrating cement was studied more than 35 years ago at the University of Illinois [Goodbrake et al. 1979]. The primary calcium silicate phases in cement were shown to react with carbon dioxide, in the presence of water, to form calcium carbonate and calcium silicate hydrate gel as shown in Equations 1 and 2:

$$3CaO \cdot SiO_2 + (3\text{-}x)CO_2 + yH_2O \rightarrow xCaO \cdot SiO_3 \cdot yH_2O + (3\text{-}x)CaCO_3 \tag{1}$$

$$2CaO \cdot SiO_2 + (2\text{-}x)CO_2 + yH_2O \rightarrow xCaO \cdot SiO_3 \cdot yH_2O + (2\text{-}x)CaCO_3 \tag{2}$$

The carbonation reactions are exothermic. The reaction proceeds in the aqueous state when Ca^{2+} ions from the cementitious phases interact with CO_3^{2-} ions from the applied gas. When the calcium silicates carbonate, the formed $CaCO_3$ is understood to be intermixed with calcium silicate hydrate (C-S-H) gel [Berger et al. 1972]. C-S-H gel formation occurs even in an ideal case of β-C_2S and C_3S exposed to a 100% CO_2 according to the observation that the amount of calcium silicate that reacts exceeds the amount that is attributable to the formation of the carbonate products [Goodbrake et al. 1979].

The reaction of carbon dioxide with a mature concrete microstructure is conventionally acknowledged to be a durability issue due to such effects such as reduced pore solution pH, and carbonation induced corrosion. In contrast, a carbonation reaction integrated into concrete production reacts CO_2 with freshly hydrating cement, rather than the hydration phases present in mature concrete, and does not have the same effects. Rather, by virtue of adding gaseous CO_2 to freshly mixing concrete the carbonate reaction products are anticipated to form in situ, are of nano-scale and homogenously distributed.

Lab work using isothermal calorimetry identified the potential performance benefit of using an optimized low dose of carbon dioxide to promote the development of finely distributed carbonate reaction products. It was concluded that a small dose of carbon dioxide could feasibly be used to provide performance benefits in ready-mixed concrete.

EXPERIMENTAL

The concept of beneficially reusing carbon dioxide through its addition to concrete was tested in an experiment conducted at a ready mix concrete facility. Carbon dioxide was delivered to ready-mixed concrete immediately after batching. Liquid CO_2 was metered for injection into the truck whereupon it converted into a mixture of gas and solid carbon dioxide "snow". The CO_2 then reacted with the hydrating cement. The concrete was then subjected to assessment and testing.

Three loads of concrete were compared: a reference mixture, a reference mixture that used a proprietary non-chloride accelerating admixture, and a load that was treated with carbon dioxide delivered over 60 seconds. The injection took place while the truck was paused at the wash rack for cleaning. Partial loads (4 m³) of concrete were batched according to the producer's standard operating procedures. The mix design

used in the trial was designed to achieve a 35 MPa compressive strength at 28 days and used a binder with 20% slag replacement of cement. The w/cm was 0.39. The mix design and admixture dosages used in the three batches are summarized in Table 1. The quantities of the admixtures are in terms of 100 kg of cementitious materials while the carbon dioxide doses are in terms of weight of carbon dioxide by weight of cement.

Table 1. Mix design and admixture loadings of the batches tested during the trial

Component	Reference	Accelerated	CO_2
Stone (kg/m^3 concrete)	1070	1070	1070
Sand (kg/m^3 concrete)	756	756	756
Cement (kg/m^3 concrete)	308	308	308
Slag (kg/m^3 concrete)	77	77	77
Retarding Water Reducer (ml/100 kg cm)	220	125	220
High Range Water Reducer (ml/100 kg cm)	200	175	175
Air entrainer (ml/100 kg cm)	23	23	23
Set accelerator (ml/100 kg cm)	-	1000	-
CO_2 (%/cement)	-	-	0.05%

The accelerator offers a water reducing effect so the producer's batching policy dictated that the retarding water reducer be decreased when the accelerator is used. The retarding water reducer reduction was not applied to the CO_2 batch. The retarding water reducer is typically anticipated to improve the concrete compressive strength. The high range water reducer dosage was slightly higher in the reference than in the other two batches but it is not typically anticipated to have any effect on compressive strength.

The production personnel manually assessed the state of the mix before making a final water adjustment to ensure that the desired consistency of the concrete was achieved prior to continuing with the testing. The batches were sampled to test the fresh properties of the concrete mixture and to prepare specimens for analysis via calorimetry, compressive strength, and various durability tests. For the batch treated with carbon dioxide the fresh properties were assessed both before and after the CO_2 addition to directly evaluate the immediate impact of the treatment.

The fresh concrete was assessed in terms of slump, air content, plastic density, temperature, initial set and final set. Isothermal calorimetry data was collected by taking 6 grams of mortar wet sieved under vibration through a 4.75mm screen and measuring the mortar's heat of hydration with a TAM Air Calorimeter. The sieved mortar was also used for time of set testing.

Concrete from each test load was used to cast 100 x 200 mm cylinders for compressive strength testing at ages of 1, 3, 7, 28, 56, 91 and 182 days. Further, test specimens for the rapid chloride penetration test (ASTM C1202), deicing salt scaling resistance (OPS LS-412: a modification of ASTM C672), freeze-thaw durability (ASTM C666), linear shrinkage (OPS LS-435: similar to ASTM C157 with 28 days drying at 50% RH after 7 days of moist curing), and hardened air void characteristics were created. Note OPS indicates Ontario Provincial Standards, as used by the highway agency in Ontario, Canada.

RESULTS

Fresh Properties. An overview of the fresh properties of each of the three batches can be found in Table 2.

Table 1. Overview of fresh properties testing

Batch	Slump before CO_2 (mm)	Slump after CO_2 (mm)	Air Content before CO_2 (%)	Air Content after CO_2 (%)	Temperature (°C)	Unit Weight (kg/m^3)
Reference	150	-	6.2	-	20.4	2372
Accelerated	135	-	5.4	-	21.0	2376
CO2	125	130	5.1	5.0	20.1	2376

The slumps, air contents, temperatures and unit weights were deemed to be acceptable, with the observed differences consistent with normal production variation. The reference batch had the highest slump, as anticipated given that it had the highest dosage of high range water reducer. The addition of carbon dioxide did not produce any change to the concrete slump or air content, as directly observed through comparison of the properties of the treated measured both before and after the CO_2 injection.

Time of Set Results. The results of the time of set testing are presented in Table 3. For each condition, the initial and final set are presented along with comparisons to the reference both in terms of the actual differences (in minutes) and as a relative comparison.

Table 3. Times of set

Batch	Initial Set			Final Set		
	Time (h)	Difference (min)	Relative to reference	Time (h)	Difference (min)	Relative to reference
Reference	7:08	-	100%	8:18	-	100%
Accelerated	4:15	-173	60%	5:36	-162	67%
CO2	5:33	-95	78%	6:34	-104	79%

The conventional accelerator cut the initial set by 173 min (a 40% reduction) and the final set by 162 min (a 33% reduction). The carbon dioxide dose cut the initial set 95 minutes (22% reduction) and the final set by 104 minutes (21% reduction). The CO_2 acceleration appeared to be less than what is provided by the conventional accelerator but an accurate comparison would acknowledge the differing admixture loading. The industrial use of the accelerator involves reducing the dose of the retarding water reducer which may thereby improve the perceived acceleration effect as it is compared to the CO_2 batch that contained the normal amount of retarding water reducer.

Calorimetry Results. The isothermal conduction calorimetry heat of hydration energy curves are presented in Figure 1.
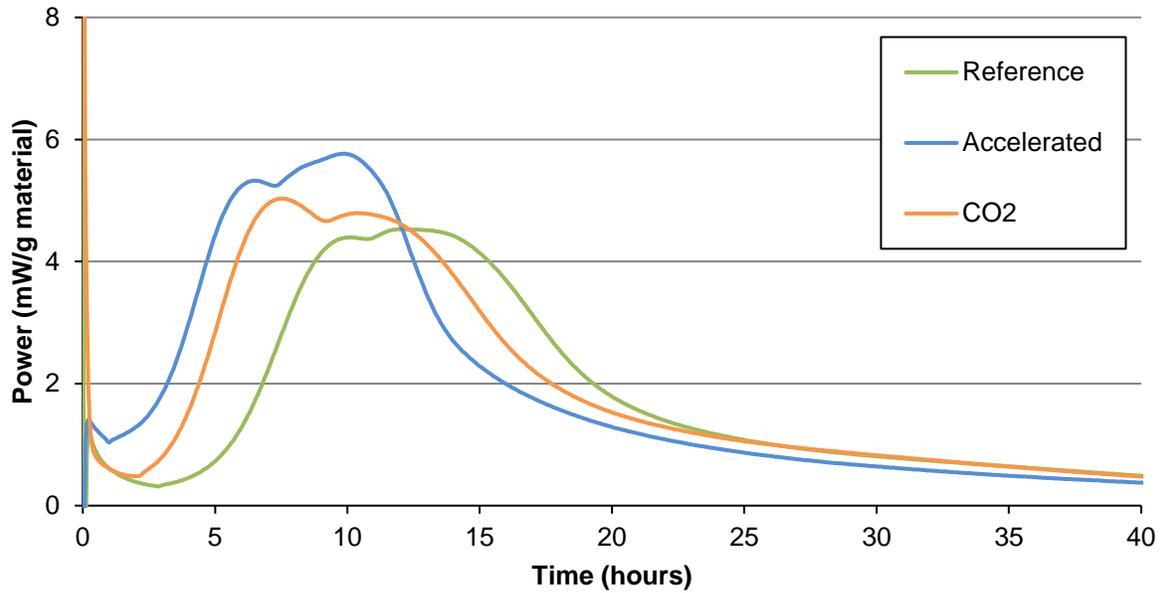
Figure 1. Conduction calorimetry of sieved mortar samples

From the power curves, as per the set time data, it can be seen that the onset of the heat evolution occurs earliest for the accelerated batch, then the CO_2 batch and then the reference. The shapes of the heat energy curves offer clues to the hydration behaviour [Jansen et al 2012]. The curve for the carbonated batch features a greater energy release for the main silicate hydration peak than for the subsequent aluminate activity peak thereby suggesting an increase in the of C_3S hydration. In the non-CO_2 injected batches, the aluminate peak is higher than the main hydration peak with a large enhancement being observed where the accelerating admixture was used.

The integration of the power curves provides the cumulative heat of hydration. The heats of hydration (presented both as J/g and relative to the reference) are summarized in Table 4.

Table 2. Overview of heat of hydration (J/g and relative to reference) at 24 of hydration.

Batch	Energy at 24 hr	Relative 24 hr
Reference	211	100%
Accelerated	252	119%
CO2	241	114%

The accelerator increased the total hydration by 19% through 24 hours. The carbon dioxide treated batch was close behind. It is notable that these two conditions were close even though the accelerated batch contained less of the retarding water reducer.

Compressive Strength Results. The results of the compressive strength testing are presented in Figure 2. For each condition the average strength values represent the average of three specimens. Relative assessments of the condition strength as compared to the reference is indicated over the appropriate bars.
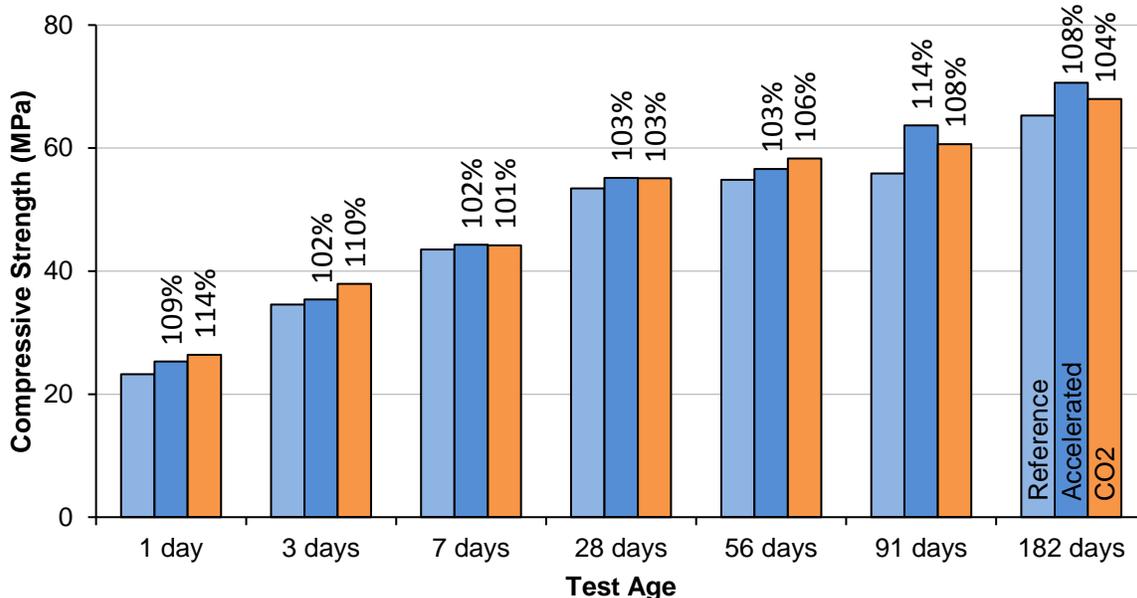
Figure 2. Compressive strength results

Compressive strength measurements of the CO_2-injected concrete batch revealed a 14% improvement of the compressive strength for the cylinders tested at 1 day and 10% at 3 days. It was functionally equivalent to the reference at ages beyond 7 days where the benefit varied between 1 and 8%.

The concrete with the dose of CO_2 proved to have a higher strength than concrete produced with the conventional accelerator at 1 and 3 days. Thereafter there was little difference between the two batches until the latter showed a 14% benefit at 91 days and 8% at 182 days.

The CO_2 utilization approach has been developed through trials at more than a dozen locations. The average strength improvements observed through a limited first-pass optimization (e.g. testing a range of dosages) were 10% at one day, 12% at three days, 11% at 7 days and 8% at 28 days [Monkman et al. 2015]. The testing examined a range of cements and SCMs and can attest to the promise of a strength benefit associated with the approach.

Linear shrinkage. The linear shrinkage tests, according to OPS LS 435, are reported in Table 4.

Table 3. Linear shrinkage test results (LS 435)

Batch	1 day	3 days	7 days	14 days	28 days
Reference	-0.005	-0.009	-0.016	-0.023	-0.033
Accelerated	-0.007	-0.011	-0.019	-0.026	-0.035
CO2-1	-0.006	-0.010	-0.017	-0.025	-0.034

All batches were found to have linear shrinkage lower than the CSA A23.1 limit for low-shrinkage concrete of 0.04% after 28-days drying at 50% RH.

Hardened air voids. The results of the hardened air void analysis are presented in Table 5.

Table 4. Hardened air void analysis results

Batch	Air content (%)	Specific Surface (mm^{-1})	Spacing Factor (mm)
Reference	4.9	38.19	0.119
Accelerated	5.0	33.33	0.134
CO2	4.3	38.49	0.130

The hardened air content and air void characteristics were acceptable for each of the batches.

A combined analysis of both the fresh and hardened air contents suggests that one caveat is applicable to the interpretation of the compressive strength. The air content (both in the fresh and hardened states) of the CO_2 batch was observed to be lower than in the reference. The strength benefits observed for this batch, as well as for the accelerated batch that had a lower fresh air content than did the reference, were possibly associated with the reductions in the air content in relation to the control condition.

Transport properties. The RCPT test results (ASTM C1202) are presented in Table 6.

Table 6. Charge passed (coulombs) in the Rapid Chloride Permeability Test (RCPT)

Batch	RCPT (coulombs)		
	28 days	56 days	180 days
Reference	1563	1061	841
Accelerated	1653	1385	906
CO2	1433	1126	965

The RCPT results suggested that the chloride ion penetrability would be low for all samples at 28 and 56 days and very low at 180 days. The CO_2 treatment did not impact the RCPT performance.

Freeze/thaw and salt scaling. The data from the ASTM C666 testing (freeze/thaw durability) and MTO LS 412 (salt scaling mass loss at 50 freeze/thaw cycles) is presented in Table 7.

Table 7. Freeze/thaw durability (ASTM C666) test results

Batch	ASTM C666 Durability Factor	ASTM C666 Mass Loss	MTO LS 412 Mass Loss
Reference	43.2%	1.66%	0.40%
Accelerated	45.5%	1.65%	0.40%
CO2	44.5%	0.84%	0.24%

That all of the durability factors calculated from loss in dynamic modulus were low, in spite of good air void spacing factors, was likely due to the lower-than-desired hardened air contents, as shown in Table 5. However, there was no negative impact of the CO_2-injection. The durability factor was comparable for the two batches without carbon dioxide and the CO_2 batch. It was observed that the batch treated with CO_2

exhibited lower mass loss in ASTM C666 than did the reference batch thereby indicating superior scaling performance.

By the conclusion of the scaling test it was observed that the batch treated with CO_2 exhibited lower scaling than did the two batches without carbon dioxide. The performance of the reference and accelerated batches was identical from 35 cycles onward. The batch with the dose of CO_2 exhibited the least scaling with a 40% reduction over the two non-CO_2 batches. It can be noted, however, that none of the samples approached the scaling limit of 0.80 kg/m^2.

DISCUSSION

The injection of carbon dioxide into concrete while mixing was associated with an increase in the energy of hydration observed through isothermal calorimetry, a reduction in the concrete set time, a neutral effect on compressive strength, and no negative effect on the durability properties.

The observed acceleration of time-of-set and early strength development with the dose of CO_2 may result from a nucleation effect. The formation of nanoscale carbonation reaction products may serve as heterogeneous nucleation sites for the precipitation of hydration products from pore solution. Seed particles acting as nuclei at a distance from cement particle surfaces have been identified as producing accelerating effects. Work with C-S-H additions (1-4% by weight) to hydrating cement systems suggested that increases in the early hydration rate and total amount of early hydration were attributable to the creation of new nucleation sites within the pore space away from the particle surfaces [Thomas et al. 2009]. Such a mechanism is particularly relevant to the reactions at hand given that they occur in solution.

Based on the tests conducted, the CO_2-injection process had a neutral to positive effect on concrete durability. Rapid chloride permeability testing performance (ASTM C1202) as well as drying shrinkage and freeze-thaw and de-icer salt scaling resistance were not negatively impacted by the CO_2-process. It should also be stated that the concrete resulting from the CO_2 injection process is not carbonated and raises no concern regarding steel corrosion. The uniformly-dispersed initial nanocarbonates that form simply act as nucleation sites that accelerate subsequent normal hydration and do not impact the later development of pore solution alkalinity.

Ex-situ additions of nano-$CaCO_3$ have been observed to achieve accelerated hydration and strength improvements [Sato and Diallo 2010; Sato and Beaudoin 2011; Bentz et al. 2012]. However, cost notwithstanding, the obstacle to integrating nano-$CaCO_3$ additions into conventional concrete is effective dispersion [Kawashima 2013]. The in-situ production of nano-scale calcium carbonate reaction products via CO_2 injection addresses this challenge.

The identified acceleration effect of the carbon dioxide, combined with lack of impact on the durability, offers an interesting prospect for use of a carbon dioxide injection alongside or instead of an accelerating admixture. Assuming a generic material cost of $350 (US) per ton of industrial carbon dioxide then the raw cost of the CO_2 used in trial would be $0.45 per truckload (10 yd^3) of concrete. As a comparison, a non-chloride accelerator cost can be estimated. The raw material cost of calcium nitrate can be taken as $130 per ton, the admixture cost as 4 times the raw material cost, and the typical admixture dosage rate as 1 to 2% by weight of cement. The cost to the concrete producer of a conventional non-chloride accelerator would be $13.50 to $27.00. Based upon a simple comparison of consumables, the carbon dioxide could offer an economic advantage over a non-chloride accelerator. Economics would potentially dictate the prospect of employing CO_2 as an accelerator or exploring a combination of CO_2 and a reduced dose of the existing accelerator.

While the strength benefit observed in the trial was limited, it can be noted that in other trials conducted at other producers a typical strength benefit of 10% was associated with the addition of carbon dioxide and that the strength increase was persistent from 24 hours to 28 days. The direct amount of carbon dioxide utilized according to the approach is small, but should a consistent strength benefit be realized there would be grounds for mix optimization that, in turn, may result in a direct environmental benefit. If the carbon dioxide could be used with a mix redesigned such that, instead of a 10% strength benefit, it would achieve 100% of the baseline strength then the unpursued strength benefit could engender reductions in the cement content, and thereby the carbon intensity, of the binder. For example, the reformulated binder could include increased proportions of SCMs or fillers.

CONCLUSION

A series of concrete mixtures were produced wherein CO_2 was injected into the freshly mixing concrete. Several notable conclusions were drawn:

- The injection of waste CO_2 into the concrete mixtures accelerated the hydration and strength development without affecting the fresh properties. The time to initial set was accelerated by 95 minutes and the final set was accelerated by 103 minutes.
- Isothermal calorimetry supported the conclusion that the CO_2 injection accelerated early hydration reactions, in particular the silicate phases. The non-chloride accelerator is normally considered to react with the aluminate phases.
- The acceleration benefits are associated with the in-situ development of uniformly distributed nano-carbonate reaction products which act as nuclei during early hydration.
- A compressive strength benefit was observed for the concrete that was treated with CO_2 but the interpretation was complicated by differences in air content (however, other trials have suggested that a strength benefit is readily achievable outcome).
- The durability testing showed that the CO_2-injection process had a neutral to positive effect on concrete durability. Suitable chloride penetration resistance, drying shrinkage, freeze-thaw, and de-icer salt scaling resistance performance of the CO_2-treated concrete was assured through testing.
- The carbon dioxide could be an economic and viable non-chloride accelerator.
- A consistent strength benefit associated with carbon dioxide addition would be a lever with which to optimize a treated mix and pursue binder blends with lower carbon intensities.

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